One particle equations for many particle quantum systems: the MCTHDF method

Claude Bardos, Norbert j. Mauser

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Abstract

This contribution is devoted to the mathematical analysis of more or less sophisticated approximations of the time evolution of systems of N quantum particles. New results for the Multiconfiguration Time Dependent Hartree Fock (MCTDHF) method (which cover the material of the talk given by the first author at the "Non linear waves conference in honor of Walter Strauss") are summarized and compared with the simpler Hartree and Hartree Fock equations.

1 Introduction, Hartree and Hartree Fock Ansatz

We deal with several types of approximations of the time dependent linear N particle Schrödinger equation. The main emphasis is put on the so called Multiconfiguration Time Dependent Hartee Fock (MCTDHF) equations, where we give a survey of recent results for the existence of unique solutions obtained in collaboration with I. Catto and S. Trabelsi [2, 3]. Also, we recall the simpler Hartree and Hartree-Fock approximations.

The starting point is the linear Schrödinger equation for the many body wavefunction $\Psi(X_N, t)$ with $X_N = (x_1, x_2, \ldots, x_N) \in \mathbb{R}^{3N}$:

$$i\hbar\partial_t\Psi = \frac{\hbar^2}{2}\sum_{1\le i\le N} H_{x_i}\Psi + \sum_{1\le j,k\le N} V^N(|x_j - x_k|)\Psi = \mathcal{H}_N\Psi \quad , \tag{1}$$

with some initial wave function $\Psi(X_N, t = 0)$ and the "one particle" Hamiltonian

$$H_x = -\frac{1}{2}\Delta_x + \mathcal{V}(t, x)\,. \tag{2}$$

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The external potential $\mathcal{V}$ and the interaction potential V^N (which may depend on N) are real which makes the Hamiltonians (essentially) self-adjoint and therefore conservation of energy and mass hold.
We normalize $\int_{\mathbb{R}^{3N}} |\Psi(X_N,t)|^2 dX = 1$.

The quantum particles are assumed to be either "bosons" , i.e. Ψ is totally symmetric with respect to its arguments) or "fermions (totally antisymmetric Ψ), a property which is obviously compatible with the flow defined by (1) (2).

In virtually all applications, however, the linear N body equation has to be reduced to (systems of) nonlinear "effective one particle equations", typically using an "ansatz" where Ψ is replaced by products of one particle wavefunctions. Best known are the Hartree equation (Schrödinger-Poisson in 3-d) as the simplest case describing Bose Einstein condensates and the Hartree-Fock equation as a simple model for fermions.

In the sequel "one particle" wave functions $\phi(x,t)$ depending on the variable $x \in \mathbb{R}^3$ are called "orbitals". Any Hilbert basis $\phi_k(x)$ of $L^2(\mathbb{R}^3)$ generates an Hilbert basis of $L^2_S(\mathbb{R}^{3N})$, the space of symmetrized L^2 functions and $L^2_\wedge(\mathbb{R}^{3N})$, the space of antisymmetrized L^2 functions. For bosons the "Hartree ansatz" yields the symmetrized basis elements

$$\Phi_\sigma(X_N) = \sum_{s\in S} \frac{1}{\sqrt{N!}} \prod_{1\le i\le N} \phi_{\sigma(s(i))}(x_i) \tag{3}$$

with σ being a map from $\{1,2,\dots,N\}$ with value in $\mathbb{N}$ and S being the set of all permutations of $\{1,2,\dots,N\}$. The particular elements of the form of a product of the same wavefunction at N different positions

$$\prod_{1\le i\le N} \phi(x_i)$$

represent Bose Einstein condensates.
For fermions, with the set $\sigma \in \Sigma_N$ of strictly increasing maps from $\{1,2,\dots,N\}$ with value in $\mathbb{N}$ (i.e. $\sigma(1) < \sigma(2) < ... < \sigma(N)$), the basis elements are the Slater determinants given by

$$\Phi_\sigma(X_N) = \frac{1}{\sqrt{N!}} \det \phi_{\sigma(j)}(x_i) \tag{4}$$

Any Hilbert basis $\phi_i(x)$ is transformed in an Hilbert basis $\phi_i(x,t)$ under the action of the "free flow"

$$e^{-it\frac{\hbar}{2}H}$$

and in the absence of interaction ($V = 0$) any function of the form (3) or (4) with time dependent $\phi_{\sigma(k)}(x_i,t)$ solutions of the "free equation:"

$$i\hbar\partial_t \phi_{\sigma(k)}(x,t) = \frac{\hbar^2}{2} H_x \phi_{\sigma(k)}(x,t) \tag{5}$$

is an exact solution of (1) and (2) . Hence the name "orbitals".
The evolution of any "pure state" wave function $\Psi(X_N,t)$ is equivalent to the

evolution of the projector $P_N(t) = \Psi(X_N, t) \otimes \overline{\Psi}(Y_N, t)$ and more generally for mixed states the density operator $D_N(0)$ (self adjoint positive operator of trace class with trace equal to 1) evolves according to the von Neumann operator equation :

$$i\hbar\partial_t D_N(t) = [\mathcal{H}_N, D_N(t)] \quad . \tag{6}$$

It is natural to introduce the n particle "density matrix" as the partial trace for $n \leq N$ which in term of the kernel of the operator is given by:

$$\begin{aligned}[D_N(t)]_{:n}(X_n, Y_n) &= \int_{(\mathbb{R}^3)^{N-n}} D_N(t)(x_1, x_2, \ldots, x_n, z_{n+1}, \ldots, z_N, \\ &\quad y_1, y_2, \ldots, y_n, z_{n+1}, \ldots, z_N) dz_{n+1}, \ldots, dz_N \, . \end{aligned} \tag{7}$$

Using the reduced density matrices for $n = 1$ up to $n = N$ a hierarchy of equations is build up, the BGGKY hierarchy.

For deriving one-particle equations the main mathematical steps are:

1 For large N replace the original N particle dynamics by simpler quantum dynamics with less microscopic information.

2 Consider the asymptotics $N \to \infty$ and $\hbar \to 0$ simultaneously, converging towards the classical Vlasov dynamics.

3 In the above process consider potentials with singular interactions including in particular the Coulomb potential.

Recently remarkable success has been achieved for the point 1 in the mean field regime where the potential felt by one particle is given by an average potential generated by the particle density in a "weak coupling scaling" i.e.

$$V_N(r) = \frac{1}{N} \tilde{V}_N \, . \tag{8}$$

The two important examples for $\tilde{V}_N$ are the case where it is constant and the case where it is a "delta sequence".

The first class of results concerns bosons in "condensed states"

$$D_N(0) = \prod_{1 \leq i \leq N} \rho(x_i, y_i, 0) = (\text{for pure states}) \prod_{1 \leq i \leq N} \phi(x_i, 0) \otimes \overline{\phi}(y_i, 0) \, . \tag{9}$$

The first marginal $[D_N(t)]_{:1}(x, y, t) = \rho(x, y, t) = \phi(x, t) \otimes \phi(y, t)$ converges to the solution the Hartree equation

$$i\hbar\partial_t \phi = H\phi + (\int_{\mathbb{R}^3} V(|x - z|)|\phi(z)|^2 dz)\phi(x) \tag{10}$$

or

$$i\hbar\partial_t \rho = [H, \rho] + [V_{1,2}, \rho(x_1, y_1, t) \otimes \rho(x_2, y_2, t)]_{:1}, \tag{11}$$

where $V_{1,2}$ is the operator of multiplication by $V(|x_1 - x_2|)$. The way to obtain such results with bounded potential was sketched by Spohn [39] and elaborated

by the authors together with Golse in [7] where the method is clearly introduced: setting up of the BGGKY hierarchy, passing to the limit as $N \to \infty$, proving uniqueness of the limit (which turns out to be technically the hardest part). Their result was extended to Coulomb like potentials (leading in particular to the Schrödinger-Poisson equation) by Erdos and Yau [18] under the hypothesis that the initial energy is bounded. This hypothesis has been removed recently by Fröhlich, Knowles and Schwartz [19].
The case of an N-dependent potential converging to a Dirac distribution leads to the derivation of the cubic non linear Schrödinger equation and was treated by Erdos, Yau and Schlein [17] for initial data with finite energy, thus deriving the Gross-Pitaeskii equation that models Bose Einstein Condensates for which the "Hartree" product ansatz of N times the same wavefunction is appropriate.

For fermions the Hartree Fock ansatz based on a Slater determinant is appropriate for initial data without correlation :

$$\Psi(X_N, 0) = \frac{1}{\sqrt{N!}} \det \, \phi_i(x_j) \, , 1 \leq i, j \leq N \, . \tag{12}$$

The mean field limit for the time dependent Hartree Fock equation is more subtle than for the Hartree case because one has (Bardos, Golse, Gottlieb and Mauser [5] :

$$D_{N:1}(0) = [\Psi(X_N, 0) \otimes \Psi(X_N, 0)]_{:1} = \frac{1}{N} \sum_{1 \leq i \leq N} \phi_i(x, 0) \otimes \overline{\phi_i(y, 0)} \tag{13}$$

and therefore $D_{N:1}(t)$ goes to zero with $N \to \infty$ in the operator norm. On the other hand its trace norm remains equal to 1 and therefore one can consider approximations $F_N(t)$ with the following properties

$$\|F_N(t)\|_{\mathrm{T}race} = \|F_N(t)\|_{\mathrm{T}race} = 1 \, , \lim_{N \to 0} \|D_{N:1}(t) - F_N(t)\|_{\mathrm{T}race} = 0 \, . \tag{14}$$

As observed in Bardos, Golse, Gottlieb and Mauser [5] and in Knowles and Fröhlich [20] this point of view shares similarities with the high frequencies approximation of oscillating solutions and in particular with the statement of Egorov theorem. The Hartree Fock equation (written in terms of the density matrix)

$$\begin{aligned} & i\hbar \partial_t F_N(x, y, t) = H_x F_N(x, y, t) - H_y F_N(x, y, t) \\ & + \int_{\mathbb{R}^3_z} (V(|x - z|) - V(|y - z|)) F_N(x, z, z) dz F_N(x, y, t) \\ & - \int_{\mathbb{R}^3_z} (V(|x - z|) - V(|y - z|)) F_N(x, z, t) F_N(z, y, t) dz \end{aligned} \tag{15}$$

provides a time dependent approximation that satisfies (14). The analysis of TDHF was given e.g. in [32] and [33], results on its derivation were first proved for bounded potential in [5, 6] and for Coulomb like potentials in [20].

Remark 1.1 *The mean field limit is much more adapted to the description of bosons than to the description of fermions with their additional "exchange interaction". This corresponds to a big loss of information in the second case. More precisely for bounded potential one has for the exchange term the estimate*

$$\begin{aligned} &\| \int_{\mathbb{R}^3_z} (V(|x-z|) - V(|y-z|)) F_N(x,z,t) F_N(z,y,t) dz \|_{\mathrm{T}race} \\ &\leq \; 2\|V\|_{L^\infty} \|F_N\|_{\mathrm{T}race} \|F_N\|_{\mathrm{O}p} \leq \frac{2}{N} \|V\|_{L^\infty} \end{aligned} \tag{16}$$

and therefore the Hartree Fock ansatz is asymptotically not better w.r.t. (14) than the Hartree ansatz.
Finally, if the initial density is bounded in energy norm:

$$\|(-\Delta) F_N(0)\|_{\mathrm{T}race} \leq C \;\; \textit{independent of } N\,.$$

Using Lieb-Thirring type inequalities one has also (even for Coulomb like potentials)

$$\lim_{N\to\infty} \| \int_{\mathbb{R}^3_z} (V(|x-z|) - V(|y-z|)) F_N(x,z,z) dz F_N(x,y,t) \|_{\mathrm{T}race} = 0 \tag{17}$$

and therefore the limit does not retain any interaction properties of the initial system and the weak coupling scaling the free evolution is left.

In the simultaneous limit $N \to \infty$ and $\hbar \to 0$, using a phase space description via the Wigner transform of $D_{N,\hbar:1}$ we can obtain Vlasov type equations :

$$\begin{aligned} &\partial_t f(x,\xi,t) + \xi \cdot \nabla_x f(x,\xi,t) \\ &-\big(\nabla_x \mathcal{V} + \int_{\mathbb{R}^3_y \times \mathbb{R}^3_\xi} \nabla_x V(|x-y|) f(y,\xi',t) d\xi' dy\big) \cdot \nabla_\xi f(x,\xi,t) = 0 \end{aligned} \tag{18}$$

which can be also derived as the limit for $N \to \infty$ of Hamiltonian equation of motion of N classical particles:

$$d_t x_i = \xi_i\,, \tag{19}$$

$$d_t \xi_i = -\nabla \mathcal{V}(x_i) - \frac{1}{N} \sum_{1 \leq i < j \leq N} \nabla_{x_i} V(|x_i - x_j|)\,. \tag{20}$$

The rigorous derivations run into serious difficulties when the potentials are singular. First results where due to Neunzert [38] and Braun and Hepp [10] with C^2 potentials. To the best of our knowledge the most refined present results are due Hauray and Jabin [28](potentials behaving like $|x|^{-\alpha}\,, \alpha < 1$ are treated with an "averaged " notion of convergence).

In agreement with this observation results for $N \to 0$ and $\hbar \to 0$ are obtained only with extra assumptions of regularity and boundedness.

With the special scaling $\hbar \sim N^{-\frac{1}{3}}$ the Vlasov dynamic (18) was recovered from the Hartree case (bosons with factorized initial data) by Narnhofer and

Sewell [37] with analytic potential and then later by Spohn [40] for C^2 potentials (cf also Golse [25] for a proof using Wasserstein distance). Observe that the Vlasov equation as a model of classical statistical mechanics cannot exhibit a difference between bosons and fermions and in agreement with the remark 1.1 Elgart Erdos Schlein and Yau have shown [15] (under technical hypothesis as analyticity of the potential and short time) that for fermions in the scaling $\hbar \sim N^{-\frac{1}{3}}$ the Vlasov limit is also recovered.

2 The MCTDHF ansatz

As remarked above convenient approximations for a system of N interacting Fermions should not rely on a mean field hypothesis. N may be large, but a $N \to \infty$ mean field limit in the weak coupling scaling does in general not correspond to the physics. The TDHF method also has the important disadvantage that by definition it cannot catch "correlations", a crucial concept for N particle quantum systems (see e.g. [26, 27]). However, by approximating Ψ by linear combinations of Slater determinants, an approximation hierarchy called Multiconfiguration time dependent Hartree Fock (MCTDHF) is obtained that allows for very precise and numerically tractable models of correlated few body systems (see e.g. [11, 43]). The MCTDHF ansatz involves a finite number $\phi_k(x,t)\,, 1 \leq k \leq K$ (with $K \geq N$) of time dependent orthonormal orbitals. With $\sigma \in \Sigma_{N,K}$ the set of strictly increasing maps from $\{1, 2, \ldots, N\}$ with value in $\mathbb{N}$ and according to the formula (4) the following expression which carries the name of Multiconfiguration Time Dependent Hartree Fock method is proposed

$$\Psi(X_N,t) = \sum_{\sigma\in\Sigma_{N,K}} c_\sigma(t)\Phi_\sigma(X_N,t) \quad \text{with } \Phi_\sigma(X_N,t) = \frac{1}{\sqrt{N!}} \det \phi_{\sigma(j)}(x_i) \tag{21}$$

where the conservation of density of particles is enforced by the relation

$$\sum_{\sigma\in\Sigma_{N,K}} |c_\sigma(t)|^2 = 1\,. \tag{22}$$

We define the space $\mathcal{F}_{N,K}$ for the $r = \binom{K}{N}$ coefficients C and the K orbitals Φ :

$$\begin{aligned} &\mathcal{F}_{N,K} = (C = \{c_\sigma(t)\}, \Phi = \{\phi_k(x,t)\}) \\ &\subset \mathcal{S}_{\ell^2(r)} \otimes L^2(\mathbb{R}^3)^K\,, (\phi_k, \phi_l) = \delta_{kl}\,, \end{aligned} \tag{23}$$

Remark 2.1 *If we would use time independent orbitals the above ansatz would lead to a "Galerkin" approximation with fixed basis functions. The use of a dynamic basis that is perfectly adapted to the problem allows to use relatively few basis functions for MCTDHF, for the prize of a quite complicated nonlinear system of equations.*
For the case $K = N$ MCTDHF can be shown to indeed coincide with TDHF described above.
With the expression (3) for the basis elements of $L_S((\mathbb{R}^3)^N)$ one can construct a

similar system for bosons, the MCTDH, but as it is described below the algebra for Fermions is simpler and leads to a natural fiber bundle.

Eventually since no semiclassical limit is involved in the sequel, to simplify the formulas, the Planck constant $\hbar$ will be taken equal to 1 and the external operator H given by the formula:

$$H_x = -\frac{1}{2}\Delta_x + \mathcal{V}(x)\,.$$

The analysis of the first and second marginals (i.e. the one- and two-particle density matrix) are essential in the description of the dynamic. They play already a role in the analysis of the preimage of the multilinear mapping π defined by (21) from $\mathcal{F}_{N,K}$ with value in $L_\wedge((\mathbb{R}^3)^N)$ and with the orthonormality of the orbitals they are given by the following formula:

Proposition 2.1 *For any $(C,\Phi)\in\mathcal{F}_{N,K}$ one has:*

$$[\Psi\otimes\Psi]_{:2}(x_1,y_1,x_2,y_2) = \sum_{ipjq}\gamma_{ipjq}\phi_i(x_1)\,\phi_p(x_2)\,\overline{\phi}_j(y_1)\,\overline{\phi}_q(y_2)\,, \quad (24)$$

$$[\Psi\otimes\Psi]_{:1}(x_1,y_1) = \sum_{ij}\gamma_{ij}\phi_i(x_1)\,\overline{\phi}_j(y_1) = \Phi\otimes\overline{\Gamma}\Phi \quad (25)$$

where the coeffcients γ_{ipjq} and $\gamma_{ij}=\sum_p\gamma_{ipjp}$ are sesquilinear forms in term of the c_σ given by the formulas:

$$\gamma_{ipjq} = \sum_{\{i\neq p\}\in\sigma\ \{j\neq q\}\in\tau\,;\sigma\setminus\{i,p\}=\tau\setminus\{j,q\}} (-1)^\sigma_{i,p}(-1)^\tau_{j,q}\,c_\sigma\,\overline{c}_\tau\,,$$

$$\gamma_{ij} = \sum_{i\in\sigma,j\in\tau\,;\{\sigma\setminus i\}=\{\tau\setminus j\}} (-1)^\sigma_i(-1)^\tau_j c_\sigma\overline{c_\tau}$$

with

$$(-1)^\sigma_{i,p} = (-1)^{\sigma^{-1}(i)+\sigma^{-1}(p)+\frac{i-p}{|i-p|}}\,;\ \ (-1)^\sigma_i = (-1)^{\sigma^{-1}(i)}\,.$$

The $K\times K$ matrix Γ defined by (25) is self adjoint non negative and with eigenvalues γ_i and one has

$$0\leq\gamma_1\leq\gamma_2\leq\ldots\leq\gamma_K\leq 1\,,\ \mathrm{Trace}(\Gamma)=N \text{ and therefore } \inf_k\gamma_k\leq\frac{N}{K}\,. \quad (26)$$

The matrix ${}^t\Gamma$ represent the action of the operator $[\Psi\otimes\Psi]_{:1}$ on the orthogonal of its kernel in the basis defined by the ϕ_k and therefore its rank coincides with the rank of this operator. The invertibility of Γ is (or the fact that the rank of $[\Psi\otimes\Psi]_{:1}$ is equal to K) is called the "full rank hypothesis" and the corresponding open subset of $(C,\Phi)\in\mathcal{F}_{N,K}$ is denoted $\partial\mathcal{F}_{N,K}$:

$$\partial\mathcal{F}_{N,K} = \left\{(C,\Phi)\in\mathcal{F}_{N,K}\setminus\ \mathrm{Rank}([\pi(C,\Phi)\otimes\pi(C,\Phi)]_{:1}) = K\right\}.$$

Given $(C_1, \Phi_1) \in \partial\mathcal{F}_{N,K}$, then for any (C_2, Φ_2) such that $\pi((C_2, \Phi_2)) = \pi((C_1, \Phi_1))$ there exists a unique unitary transform $U \in O(\mathbb{C}^K)$ such that, with

$$\mathcal{U}^*_{\sigma,\tau} = \det\,(U_{\sigma(i),\tau(j)}) \text{ and } \mathbf{U} = (\mathcal{U}, U)\,,$$

one has

$$(C_2, \Phi_2) = \mathbf{U}(C_1, \Phi_1).$$

The set $\mathcal{O} = \{(\mathcal{U}, U)\}$ is a transitive unitary group and the relation

$$\pi(\partial\mathcal{F}^{FR}_{N,K}) = \partial\mathcal{F}^{FR}_{N,K}/\mathcal{O}$$

induces a structure of fiber bundle. In agreement with the physical intuition and in particular the fact that they are determined in term of different systems of orbitals the elements of $\mathcal{O}$ carry the name of gauge transformations.

3 Two flows on the Full Rank Fiber Bundle

The time evolution of the MCHF ansatz is given by a complicated nonlinear system of $\binom{K}{N}$ ODEs + K PDEs for the coefficients C and the orbitals Φ that are related to the wavefunction by

$$\Psi(X_N, t) = \pi(C(t), \Phi(t) = \sum_\sigma c_\sigma(t)\Phi_\sigma(X_N, t) \tag{27}$$

For $\Psi(X_N, t) \in \partial\mathcal{F}_{N,K}$ we use the MCTDHF equations in the formulation of the following system which has been named "working equations" by Scrinzi et al. [11].

$$\begin{aligned} i\frac{d}{dt}c_\sigma(t) &= \langle(\sum_{1\le i<j\le N} V(|x_i - x_j|)\Psi)\ , \Phi_\sigma\rangle\,, \\ i\frac{\partial\Phi(t,x)}{\partial t} &= H\Phi(t,x) + \Gamma(t)^{-1}(I - \mathcal{P}_\Phi)([\nabla_\Phi\ \Psi]^\star V\Psi) \end{aligned} \tag{28}$$

with H and $\mathcal{P}_\Phi$ two diagonal operators given by the formulas:

$$H = \left(-\frac{1}{2}\Delta + \mathcal{V}\right) \otimes I_K\ ,\ \mathcal{P}_\Phi = \sum_{1\le k\le K} (., \phi_k)\phi_k(x,t) \otimes I_K\,.$$

Since the mapping $\pi : (C, \Phi) \mapsto \Psi$ is multilinear its gradient is well defined and $[\nabla_\Phi\ \Psi]^\star$ is a linear continuous operator from $L^2_\wedge(\mathbb{R}^{3N})$ with value in $L^2(\mathbb{R}^3)^K$. Eventually one has

$$[\nabla_\Phi\ \Psi]^\star\ V\ \Psi = \sum_{1\le p,q\le K} \gamma_{ipjq} \int_{\mathbf{R}^3} \overline{\phi}_p(t,y)\, V(|x-y|)\, \phi_q(t,y)\, dy.$$

The working equations are well adapted for local in time proof of existence and stability. To obtain global in time information and use the physical intuition it

is convenient to associate to these equations an other system which we call the "variational system":

$$i\frac{d}{dt}c'_\sigma(t) = \langle \mathcal{H}\ \Psi' \mid \Phi'_\sigma \rangle\,, \tag{29}$$

$$i\Gamma(t)\ \frac{\partial}{\partial t}\Phi'(t,x) = (I - \mathcal{P}_{\Phi'})[[\nabla_{\Phi'}\ \Psi']^\star\ \mathcal{H}\ \Psi']\,. \tag{30}$$

Solutions of the "working equation" and of the "variational system" are related by a gauge transformation according to the following:

Proposition 3.1 *Let $(C(t), \Phi(t)) \in \partial\mathcal{F}_{N,K}$ be a solution of the "working equation" then the formulas:*

$$U(0) = Id\,,\ i\frac{dU}{dt} = -U(t)M(t)\,,\ \textit{with}\ (M(t))_{ij} = \frac{1}{2}(H\phi_i(t), \phi_j(t))$$

and

$$\mathcal{U}(t)^*_{\sigma,\tau} = \ \det\left(U_{\sigma(i),\tau(j)}(t)\right),\ \mathbf{U}(t) = (\mathcal{U}(t), U(t)) \tag{31}$$

define a gauge transformation

$$(C(t), \Phi(t)) \mapsto (C'(t), \Phi'(t)) = (\mathcal{U}(t)C(t), U(t)\Phi(t))$$

which preserve the fiber ($\pi(C'(t), \Phi'(t)) = \pi(C(t), \Phi(t))$) and which transform the solution of the workings equations into the solution of the "variational system"

As a consequence as long as one of the two systems of equations has a smooth solution the same is true for the other. The name given to the second systems comes from the fact that this system is equivalent to the Dirac Frenkel variational principle

$$\langle [i\frac{\partial}{\partial t} - \mathcal{H}]\Psi' | \delta\Psi' \rangle = 0, \tag{32}$$

for all variation $\delta\Psi'$ in the tangent space to $\partial\mathcal{F}_{N,K}$. From (32) with $\partial_t\Psi' = \delta\Psi'$ one deduces the conservation of energy:

$$\langle [i\frac{\partial}{\partial t} - \mathcal{H}]\Psi | \frac{\partial\Psi}{\partial t} \rangle = 0 \Rightarrow Re\langle \mathcal{H}\Psi, \frac{\partial\Psi}{\partial t} \rangle = 0 \Rightarrow \frac{d\mathcal{E}(\Psi)}{dt} = 0 \tag{33}$$

with

$$\begin{aligned}\mathcal{E}(\Psi) &= \frac{1}{2}\langle \mathcal{H}\Psi, \Psi \rangle \\ &= \int_{\mathbb{R}^3} ((\Gamma\nabla\Phi, \nabla\Phi) + \mathcal{V}(x)[\Psi \otimes \Psi]_{:1}(x,x))dx \\ &+ \int_{\mathbb{R}^3_x \times \mathbb{R}^3_y} V(|x-y|)[\Psi \otimes \Psi]_{:2}(x,y,x,y))dxdy\,.\end{aligned} \tag{34}$$

With the full rank hypothesis the projection on the tangent space to $\partial\mathcal{F}_{N,K}$: $\mathcal{P}_{\mathbf{T}}(\partial\mathcal{F}_{N,K})$ is continuous. With (32) this leads to an a-posteriori error estimate according to the

Proposition 3.2 *For any pair $\Psi_E(t)$ exact solution of the N particles Schrodinger equation and $\Psi(t) = \pi(C(t), \Phi(t))$ with $(C(t), \Phi(t)) \in \partial\mathcal{F}_{N,K}$ smooth solution of the "variational system" (or of the working equations) one has the following stability estimate:*

$$\|\Psi_E - \Psi\|_{L^2(\Omega^N)} \leq \|\Psi_E^0 - \Psi^0\|_{L^2(\Omega^N)} + |\int_0^t (I - \mathcal{P}_{\mathbf{T}(\partial\mathcal{F}_{N,K})} [\mathcal{H}\,\Psi(s)]\, ds|. \quad (35)$$

Remark 3.1 *The proof left to the reader is a direct consequence of (32); It is a a-posteriori error estimate. Intuitively the term*

$$(I - \mathcal{P}_{\mathbf{T}(\partial\mathcal{F}_{N,K})})$$

should go to zero in operator norm (for N fixed and $K \to \infty$) however a precise estimate does not seems easy to obtain.

4 Analysis of the Cauchy problem

This section is devoted to the analysis of the Cauchy Problem for the MCTDHF; The main sources of difficulties are the fact the matrix $\Gamma(t)$ may degenerate and that the physical potentials are singular. In the sequel these potentials are assumed to be given by the formula

$$\mathcal{V} = \sum_{m=1}^{M} \frac{z_m}{|x - R_m|}\,,\ V(|x-y|) = \frac{1}{|x-y|}\,, \quad (36)$$

and one has:

$$\mathcal{H} = \sum_{1\leq i\leq N} -\frac{1}{2}\Delta_{x_i} + V(x_i) + \sum_{1\leq i<j\leq N} V(|x_i - x_j|)\,. \quad (37)$$

With (36) and (37) $\mathcal{H}$ is an unbounded selfadjoint operator in $L^2(\mathbb{R}^{3N})$ with spectra bounded from below by a constant $\sigma(\mathcal{H})$. The working equation is written in "Duhamel" form according to the formula:

$$U(t) = e^{-it\mathcal{A}}U_0 - i\int_0^t e^{-i(t-s)\mathcal{A}} L(U)(s) ds \quad (38)$$

with

$$U(t) = \begin{pmatrix} C \\ \Phi(t) \end{pmatrix}, \mathcal{A} = \begin{pmatrix} 0 \\ H \otimes I_K \end{pmatrix}, \quad (39)$$

and

$$L(U)(t) = \begin{pmatrix} \langle (\sum_{1\leq i<j\leq N} V(|x_i - x_j|)\Psi(t))\ , [\Phi_\sigma](t)\rangle\,. \\ \\ \Gamma(t)^{-1}(I - \mathcal{P}_\Phi)([\nabla_\Phi\ \Psi]^\star V(t) \end{pmatrix} \quad (40)$$

On the set

$$\partial\mathcal{F}^1{}_{N,K} = \{(C,\Phi) \in \partial\mathcal{F}_{N,K} \text{ with } \Phi \in (H^1(\mathbb{R}^3))^K\}\,,$$

equipped with the topology of $\mathcal{S}_{\ell^2(r)} \otimes (H^1(\mathbb{R}^3)^K)$, the operator L is locally Lipschitz (the H^1 regularity compensates the singularity of the potential). Hence the Cauchy problem written in term of strong solution (formula (38)) has for any $U_0 = (C_0, \Phi_0) \in \partial\mathcal{F}^1_{N,K}$ a unique local in time solution. Since the working equations are equivalent to the variational system, the energy is conserved. Hence the H^1 norm of the orbitals remains bounded as long as the density matrix $\Gamma(t)$ does not degenerates. This give the following

Proposition 4.1 *For any initial data $(C_0, \Phi_0) \in \partial\mathcal{F}^1{}_{N,K}$ the working equations have a unique strong solution $(C(t), \Phi(t)) \in C(0, T^*, \mathcal{S}_{\ell^2(r)} \otimes (H^1(\mathbb{R}^3)^K))$ on a maximal interval $[0, T^*[$. Furthermore*

$$T^* < \infty \Rightarrow \overline{\lim_{t \to T^*}} \|\Gamma(t)^{-1}\| = \infty\,. \tag{41}$$

Remark 4.1 *For $K = N$ the density matrix $\Gamma(t)$ is I_N, so it can never degenerate, and therefore with the hypothesis of the proposition 3.1 one has a global in time solution. Moreover*

$$\begin{aligned}
&([\nabla_\Phi\, \Psi]^\star V\Phi)_i = \\
&\sum_{1\le j\le N} \int_{\mathbf{R}^3} V(x-y)|\phi_j(t,y)|^2 dy \phi_i(t,x) \\
&- \sum_{1\le j\le N} \int_\Omega V(x-y)\phi_i(t,y)\overline{\phi}_j(t,y)\phi_j(t,x)dy
\end{aligned} \tag{42}$$

and the working equations for the orbitals are:

$$i\frac{\partial\Phi(t,x)}{\partial t} = H\Phi(t,x) + (I - \mathcal{P}_\Phi)K_\Phi\Phi \tag{43}$$

with

$$\begin{aligned}
K_\Phi(w) &= \int_{\mathbf{R}^3} V(|x-y|) \sum_{1\le j\le N} |\phi_i(y)|^2 dy w(x) \\
&- \int_{\mathbf{R}^3} V(x-y)(\sum_{1\le j\le N} \overline{\phi_j(y)}\phi_j(x))w(y)dy\,.
\end{aligned} \tag{44}$$

Observe that K_Φ is self adjoint , introduce the self adjoint matrix

$$M(t) = ((M(t))_{ij} = (K_\Phi(\phi_i(t)), \phi_j(t)))\,.$$

and rewrite (43) to obtain:

$$i\frac{\partial\Phi(t,x)}{\partial t} = H\Phi(t,x) + K_\Phi\Phi - M(t)\Phi\,.$$

Then the equation:

$$U(0) = Id\,,\ i\frac{dU}{dt} = -U(t)M(t)\,,\ \textit{with}$$

defines a unitary matrix and a gauge transformation which changes the equation (43) into the classical Hartree Fock equation presented in the section 1. Thus one recover in this case the well posedness global in time H^1 result of Chadam Glassey (1975)) [13].

The conservation of the invertibility of the matrix $\Gamma(t)$ being an essential issue in the MCTDHF it is natural to give sufficient condition for such property. For any $K \geq N$ one introduces the "$K-$ground state energy":

$$\mathcal{I}(K) = \inf_{(C,\Phi)\in\mathcal{F}_{N,K}} (\mathcal{H}\pi(C,\Phi)), \pi(C,\Phi))\,. \tag{45}$$

Obviously one has:

$$\sigma(\mathcal{H}) = \inf_{|\Psi|=1} (\mathcal{H}\Psi,\Psi) \leq \mathcal{I}(K) \text{ and } K' \geq K \Rightarrow \mathcal{I}(K') \leq \mathcal{I}(K)\,. \tag{46}$$

Theorem 4.1 *For any $(C_0,\Phi_0) \in \partial\mathcal{F}^1_{N,K}$ the relation*

$$\mathcal{E}(\pi(C_0,\Phi_0)) = (\mathcal{H}\pi(C_0,\Phi_0), \pi(C_0,\Phi_0)) < \mathcal{I}(K-1) \tag{47}$$

implies the global in time invertibility of the matrix Γ hence the global in time existence of a strong solution.

Remark 4.2 *The hypothesis $\sum z_m \geq N$ in (36) implies (cf. [23] and [29]) the relation $\mathcal{I}(K) < \mathcal{I}(K-2)$). Therefore (47) can be always satisfied by changing K into $K-1$.*

The proof is done by contradiction assuming the existence of a first finite time T^* where the matrix $\Gamma(t)$ degenerates. This implies, for its eigenvalues, arranged in decreasing order

$$0 \leq \gamma_K \leq \gamma_{K-1} \leq \ldots \leq \gamma_1 \leq 1\,,$$

the existence of a sequence t_n converging to $T^\star$ with a positive number β and an integer $N+1 \leq m \leq K$ such that

$$\lim_{n\to+\infty} \gamma_m(t_n) = 0 \quad \text{and} \quad 0 < \beta \leq \gamma_{m-1}(t_n)\,. \tag{48}$$

Introduce the gauge transformation $\mathbf{U}_n = (\mathcal{U}_n, U_n)$ with U_n which diagonalizes $\Gamma(t_n)$: With $(C'_n,\Phi'_n) = \mathbf{U}_n(C(t_n),\Phi(t_n)$ one has:

$$\Psi(t_n) = \sum_\sigma c_\sigma(t_n)\Phi(t_n) = \sum_\sigma c'_\sigma(t_n)\Phi'_n \tag{49}$$

The primed variable are used in the sequel (and the primes are omitted), wave and energy are expressed in these new variables according to the formulas

$$\Psi^n = \Psi_n^- + \Psi_n^+ ,$$
$$\Psi_n^- = \sum_{\sigma\cap\{m,m+1,\dots,K\}\neq\emptyset} c_\sigma^n \Phi_\sigma^n ,$$
$$\Psi_n^+ = \sum_{\sigma\cap\{m,m+1,\dots,K\}=\emptyset} c_\sigma \Phi_\sigma^n .$$

$$\mathcal{E}(\pi(C_n,\Phi_n)) = \sum_{1\le i\le K}\int_{\mathbf{R}^3} \gamma_i^n(\frac{1}{2}|\nabla\phi_i^n|^2 + \mathcal{V}|\phi_i^n|^2)dx +$$
$$\sum_{ijkl}\gamma_{ijkl}\int_{\mathbf{R}^3\times\mathbf{R}^3}\frac{1}{|x-y|}\phi_i(x)\overline{\phi_k(y)}\phi_j(y)\overline{\phi_l(x)}dxdy . \tag{50}$$

Since the matrix Γ_n now is diagonal one has:

$$\gamma_i = \sum_{i\in\sigma}|c_\sigma|^2 \tag{51}$$

and therefore the hypothesis (48) implies the relations:

$$\sigma\cap\{m,m+1,\dots,K\}\neq\emptyset \Rightarrow \lim c_\sigma = 0 , \tag{52}$$
$$\text{and } \{i,j,k,l\}\cap\{m,\dots,K\}\neq\emptyset \Rightarrow \lim\gamma_{ijkl} = 0 . \tag{53}$$

This has the following consequences:

1 Φ_n^- converges strongly to zero in $L^2(\mathbb{R}^{3N})$.

2 With the relation (50) and the standard "Kato inequalities" the functions $\sqrt{\gamma_n}\nabla\phi_k(n)$ are uniformly bounded in $L^2(\mathbf{R}^{3N})$ and therefore (cf [2] and [3] for details)

$$\mathcal{E}(\Psi_0) = \mathcal{E}(\Psi_n) \ge \liminf_{n\to\infty}\mathcal{E}(\Psi_n^+) . \tag{54}$$

Next observes that

$$\lim_{n\to\infty}\|\Psi_n^+\|_{L^2(\mathbb{R}^{3N})} = \sum_{\sigma\cap\{m,m+1,\dots,K\}=\emptyset}|c_\sigma|^2 = 1 \tag{55}$$

and that

$$\frac{\Psi_n^+}{\|\Psi_n^+\|_{L^2(\mathbb{R}^{3N})}} \in \partial\mathcal{F}_{N,m-1} .$$

Eventually, the energy being quadratic with respect to Ψ, one has:

$$\mathcal{E}(\Psi_n^+) = \|\Psi_n^+\|^2_{L^2(\mathbb{R}^{3N})}\mathcal{E}(\frac{\Psi_n^+}{\|\Psi_n^+\|_{L^2(\mathbb{R}^{3N})}}) \ge \|\Psi_n^+\|^2_{L^2(\mathbb{R}^{3N})}I(m-1) . \tag{56}$$

With the relation (55) the contradiction comes (with $m-1<K$ and $I(m-1)\ge I(K)$) from the estimates:

$$I(K) > \mathcal{E}(\Psi_0) = \mathcal{E}(\Psi_n) \ge \liminf_{n\to\infty}\mathcal{E}(\Psi_n^+) = I(m-1) . \tag{57}$$

5 Stabilisation of Γ and Strichartz estimates

Even if as above the density matrix Γ does not degenerate its eigenvalues may come close to 0 . Observe, in particular, that with the relation $\mathrm{Trace}(\Gamma(t)) = N$ the smallest eigenvalue is less that NK^{-1} and that for K large the system becomes "stiff". Therefore it is natural to regularise the matrix $\Gamma(t)$ (cf. [8]).

The working equations become:

$$i\frac{d}{dt}c_\sigma(t) = \langle (\sum_{1\le i<j\le N} V(x_i - x_j)\Psi)\ , \Phi_\sigma\rangle\,, \tag{58}$$

$$\Gamma_{ij}(t) = \gamma_{ij} = \sum_{i\in\sigma, j\in\tau\ ;\{\sigma\setminus i\}=\{\tau\setminus j\}} (-1)^\sigma_i (-1)^\tau_j c_\sigma(t)\overline{c_\tau(t)}\,, \tag{59}$$

$$\Gamma_\epsilon(t) = \Gamma(t) + \epsilon(e^{-\frac{\Gamma}{\epsilon}})\,, 10^{-8} \le \epsilon \le 10^{-4}\,, \tag{60}$$

$$i\Gamma_\epsilon(t)\frac{\partial\Phi(t,x)}{\partial t} = \Gamma_\epsilon(t)H\Phi(t,x) + (I - \mathcal{P}_\Phi)([\nabla_\Phi\ \Psi]^\star V\Psi)\,. \tag{61}$$

In (60) Γ_ϵ is given by a formula which acts only on the "small" eigenvalues": on $\mathrm{Ker}(\Gamma$)the regularisation is of the order of ϵ ; on $\mathrm{Ker}(\Gamma)^\perp$ it behaves like $O(\epsilon^\infty)$. In this regularisation the global invertibility of the matrix Γ_ϵ is enforced but since the exact matrix Γ comes from the Dirac Frenkel variational principle the above system does not conserves anymore the energy and the H^1 lipschitz property of the non linear term useful for Coulomb like potentials $\mathcal{V}$, V provides only local in time results. The only global in time conserved quantity is related to the density of particles

$$\sum_\sigma |c_\sigma(t)|^2 = 1\,, \int_{\mathbf{R}^3} |\phi_k(x,t)|^2 dx = 1$$

and is of L^2 types. Therefore use of Strichartz estimates turns out to be the natural tool. As in the previous section (and with the same notations) one writes the perturbed working equation in "Duhamel " form

$$c_\sigma(t) = c_\sigma(0) + \int_0^t \langle (\sum_{1\le i<j\le N} V(x_i - x_j)\Psi)\ , \Phi_\sigma\rangle(s)ds\,,$$

$$\Phi(t) = e^{-it\frac{1}{2}\Delta}\Phi(0) + \int_0^t e^{-i(t-s)\frac{1}{2}\Delta}(\mathcal{V}\Phi(s)\,,$$

$$+(\Gamma_\epsilon(t))^{-1}(I - \mathcal{P}_\Phi)([\nabla_\Phi\ \Psi]^\star V\Psi)(s)ds,\,.$$

The potentials $\mathcal{V}$ and $V(|x|)$ belong to $L^{\frac{3}{2}} + L^\infty$. Therefore, following Zagatti [42] and Castella [12], one introduces, with $q = \frac{2d}{d-1} < 6$ and $\frac{2}{3p} = (\frac{1}{2} - \frac{1}{q})$, the spaces

$$X_T = (L^\infty(0,T;\mathcal{S}_{\ell^2(r)}) \otimes ((L^\infty(0,T;L^2(\mathbf{R}^3)) \cap (L^p(0,T;L^q(\mathbf{R}^3)))^K\,. \tag{62}$$

With Strichartz estimate and interpolation one has

$$\|e^{-it\frac{1}{2}\Delta}\Phi(0)\|_{L^p(0,T;L^q(\mathbf{R}^3)))^K} \leq C(q)T^{\frac{3}{q}-\frac{1}{2}}$$

and therefore, for $R > 0$ and $T < T^*$ small enough, the non linear operator $U = (C, \Phi) \mapsto L(U)$ which appears in the "Duhamel" integral term

$$L(U)(t) = \begin{pmatrix} \int_0^t \langle (\sum_{1\leq i<j\leq N} V(|x_i - x_j|)\Psi(s)) \, , [\Phi_\sigma](t)\rangle ds \\ \\ \int_0^t e^{-i(t-s)\frac{1}{2}\Delta}(\mathcal{V}\Phi(s) + (\Gamma_\epsilon(t))^{-1}(I - \mathcal{P}_\Phi)([\nabla_\Phi \, \Psi]^\star V\Psi)(s)ds) \end{pmatrix}$$

maps the ball of radius R of

$$X_T = (L^\infty(0,T;\mathcal{S}_{\ell^2(r)}) \otimes ((L^\infty(0,T;L^2(\mathbf{R}^3)) \cap (L^p(0,T;L^q(\mathbf{R}^3)))$$

in itself and is lipschitzian with a lipschitz constant bounded by

$$C(\Gamma_\epsilon, \|\mathcal{V}\|_{L^d}, \|V\|_{L^d})R^5 T^{\frac{3}{q}-\frac{1}{2}} \, . \tag{63}$$

In (63) the constant depends only on the L^2 norm of the solution (which by conservation is bounded by 1). Then existence and uniqueness of a strong solution in X_∞ with no assumption on the H^1 norm follows by iteration from $[0, T^*[$ to $[T^*, 2T^*[$ and so on ... This is summarised in the

Proposition 5.1 *For any initial data $(C_0, \Phi_0) \in \partial\mathcal{F}_{N,K}$ the $\epsilon > 0$ regularised working equation admits a unique strong solution*

$$(C(t), \Phi(t)) \in (L^\infty(0,\infty;\mathcal{S}_{\ell^2(r)}) \otimes ((L^\infty(0,\infty;L^2(\mathbf{R}^3)) \cap (L^p_{\rm loc}(0,\infty;L^q(\mathbf{R}^3))) \, .$$

Eventually one should hope that if the original solution is well defined (with density matrix $\Gamma(t)$ non degenerate) on a time interval $0 \leq t < T^*$ it will be on the same interval the limit for $\epsilon \to 0$ of the solution of the perturbed working equations. This is the object of the

Theorem 5.1 *Let $(C_0, \Phi_0) \in \partial\mathcal{F}^1_{N,K}$ and consider the solution of the perturbed working equations (58),(59)*

$$\begin{aligned} U_\epsilon(t) &= (C_\epsilon(t), \Phi_\epsilon(t)) \\ &\in (L^\infty(0,\infty;\mathcal{S}_{\ell^2(r)}) \otimes ((L^\infty(0,\infty;L^2(\mathbf{R}^3)) \cap (L^p_{\rm loc}(0,\infty;L^q(\mathbf{R}^3))) \end{aligned} \tag{64}$$

Assume that $U(t) = (C(t), \Phi(t))$ the solution (with the same initial data) of the original "working equations" is well defined on $0, T^*$ ie

$$\sup_{0<t<T^*} \|(\Gamma(t))^{-1}\| \leq C < \infty \, .$$

Then for $\epsilon > 0$ small enough

$$U_\epsilon(t) = (C_\epsilon(t), \Phi_\epsilon(t) \in C(0, T^\epsilon; \mathcal{S}_{\ell^2(r)}) \otimes H^1(\mathbb{R}^3)^K) \tag{65}$$

and converge to $U(t)$ in the same norm denoted $\|.\|_1$.

The proof (cf [3]) is inspired by standard demonstrations of shadowing lemma. Once again the problems are written for $\epsilon \geq 0$ in "Duhamel" form:

$$U_\epsilon(t) = e^{-it\mathcal{A}}U_0 - i\int_0^t e^{-i(t-s)\mathcal{A}}L_\epsilon(U_\epsilon)(s)ds\,. \tag{66}$$

The operators L_ϵ being locally Lipschitzian on $\mathcal{S}_{\ell^2(r)}) \otimes H^1(\mathbb{R}^3)^K$, for t small enough one has also $U_\epsilon(t) \in \mathcal{S}_{\ell^2(r)}) \otimes H^1(\mathbb{R}^3)^K$ (The perturbed Cauchy problem is solved locally in time). For $\eta > 0$ introduce the maximal time $0 < T_\epsilon \leq T^*$ such that

$$\forall t \in [0, T_\epsilon]\,, \|U_\epsilon(t) - U(t)\|_1 \leq \eta \tag{67}$$

Since the operator L_ϵ is locally lipschitzian for $\eta < \eta_0$ small enough (independent of ϵ) and $0 \leq t \leq T_\epsilon \leq T^*$ there exists a constant such that

$$\begin{aligned} &\|U_\epsilon(t) - U(t)\|_1 \leq \eta \\ &\Rightarrow \|L_\epsilon(U_\epsilon(t)) - L(U(t))\|_1 \leq C(\eta, U(t))(\|U_\epsilon(t) - U(t)\|_1 + \epsilon)\,. \end{aligned} \tag{68}$$

With (66) and the Gronwall estimate, this in turn implies that in the same interval one has

$$\|U_\epsilon(t) - U(t)\|_1 \leq \epsilon C(\eta, U(t))e^{C(\eta,U(t))t}\,. \tag{69}$$

With

$$\epsilon < \frac{1}{C(\eta, U(t))}e^{-C(\eta,U(t))T^*}$$

this implies by a contradiction argument that $T_\epsilon = T^*$ Eventually (69) remains valid for $t < T^*$ and the convergence follows.

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References

[1] R. Adami, F. Golse, A. Teta, Rigorous derivation of the cubic NLS in dimension one. *J. Stat. Phys.* **127** no. 6, 1193–1220 (2007)

[2] C. Bardos, I. Catto, N.J. Mauser and S. Trabelsi, Global-in-time existence of solutions to the multi-configuration time-dependent Hartree-Fock equations: A sufficient condition. *Applied Math. Lett.* **22**, 147–152 (2009)

[3] C. Bardos, I. Catto, N.J. Mauser and S. Trabelsi, Setting and analysis of the multi-configuration time-dependent Hartree-Fock equations. *manuscript* (2009)

[4] C. Bardos, L. Erdös, F. Golse, N.J. Mauser and H.-T. Yau, Derivation of the Schrödinger-Poisson equation from the quantum N-particle Coulomb problem, *C. R. Acad. Sci., t 334 (6) Série I Math.* (2002) 515-520.

[5] C. Bardos, F. Golse, A. Gottlieb and N.J. Mauser, Mean-field dynamics of fermions and the time-dependent Hartree–Fock equation. *J. Math. Pures et Appl.* **82**, 665–683 (2003)

[6] C. Bardos, F. Golse, A. Gottlieb and N.J. Mauser, Accuracy of the time-dependent Hartree-Fock approximation for uncorrelated initial states. *Journal of Statistical Physics* **115** (3-4), 1037–1055 (2004)

[7] C. Bardos, F. Golse and N.J. Mauser, Weak coupling limit of the N-particle Schrödinger equation. *Methods Appl. Anal. 7* **2**, 275–293 (2000)

[8] M. Beck, A. H. Jäckle, G.A. Worth and H. -D. Meyer, The multi-configuration time-dependent Hartree (MCTDH) method: a highly efficient algorithm for propagation wave-packets. *Phys. Rep.,* **324**, 1–105 (2000)

[9] A. Bove, G. Da Prato and G. Fano, On the Hartree-Fock time-dependent problem. *Comm. Math. Phys.* **49**, 25–33 (1976)

[10] W. Braun and K. Hepp, The Vlasov Dynamics and its fluctuation in the 1/N limit of interacting particles, *Comm. Math. Phys.* 56 (1977), 101–113.

[11] J. Caillat, J. Zanghellini, M. Kitzler, O. Koch, W. Kreuzer and A. Scrinzi, Correlated multi-electron systems in strong laser fields – An MCTDHF approach. *Phys. Rev. A*, **71**, 012712 (2005)

[12] F. Castella, L^2 solutions to the Schrödinger–Poisson system: existence, uniqueness, time behavior, and smoothing effects. *Math. Models Methods Appl. Sci.* **7** (8), 1051–1083 (1997)

[13] J.M. Chadam and R.T. Glassey, Global existence of solutions to the Cauchy problem for the time-dependent Hartree equation. *J. Math. Phys.* **16**, 1122–1230 (1975)

[14] A.J. Coleman, Structure of Fermion Density Matrices. *Rev. Mod. Phys.* **35**(3), 668–689 (1963)

[15] A. Elgart, L. Erdös, B. Schlein, H.-T. Yau, Non linear Hartree equation as the mean field limit of weakly coupled fermions *J. Math. Pures et Appl.* bf 83 (2004), no. 2, 1241–1273.

[16] A. Elgart, L. Erdös, B. Schlein, H.-T. Yau, Gross-Pitaevskii equation as the mean field limit of weakly coupled bosons. *Arch. Ration. Mech. Anal* **179** (2006), no. 2, 265–283.

[17] L. Erdös, B. Schlein, H.-T. Yau, Derivation of the cubic non-linear Schrödinger equation from quantum dynamics of many-body systems. *Invent. Math.* **167** (2007), no. 3, 515–614.

[18] L. Erdös and H.-T. Yau, Derivation of the nonlinear Schrödinger equation with Coulomb potential. *Advances in theoretical math. physics.* (2003)

[19] J. Fröhlich, A. Knowles, S. Schwarz, On the Mean-Field Limit of Bosons with Coulomb Two-Body Interaction. *preprint* arXiv: 0805.4299v1 [math-ph] 28 May 2008.

[20] J. Fröhlich, A. Knowles, A Microscopic Derivation of the Time-Dependent Hartree-Fock Equation with Coulomb Two-Body Interaction. *preprint* arXiv:0810.4282v1

[21] J. Frenkel, Wave Mechanics, Oxford University Press, Oxford (1934)

[22] G. Friesecke, The multi-configuration equations for atoms and molecules: charge quantization and existence of solutions. *Arch. Rational Mech. Anal.* **169**, 35–71 (2003)

[23] G. Friesecke, On the infinitude of non-zero eigenvalues of the single-electron density matrix for atoms and molecules. *R. Soc. Lond. Proc. Ser. A Math. Phys. Eng. Sci.* **459**(2029), 47–52 (2003)

[24] J. Ginibre and G.Velo, On a class of nonlinear Schrödinger equations with non-local interaction. *Math. Z.* **170**, 109–136 (1980)

[25] F. Golse, On the mean field limit for large particle systems, *actes du colloque du GdR Equations aux derivees partielles, Forges-les-Eaux* (2006)

[26] A. Gottlieb and N.J. Mauser, A new measure of correlation for electron systems, *Phys. Rev. Lett.* **95 (12)** 1230003 (2005)

[27] A. Gottlieb and N.J. Mauser, Properties of non-freeness: an entropy measure of correlation of electrons, *Int. J. of Quantum Information* **5**(6) (2007) 10 n:33.

[28] M. Hauray, P.E. Jabin, N-particles approximation of the Vlasov-Poisson equation, *Arch. Ration. Mech. Anal.* **183**, 489–524 (2007).

[29] C. Le Bris, A general approach for multi-configuration methods in quantum molecular chemistry. *Ann. Inst. H. Poincaré Anal. Non Linéaire* **11**(4), 441–484 (1994)

[30] O. Koch and C. Lubich, Regularity of the Multi-Configuration Time-Dependent Hartree Approximation in Quantum Molecular Dynamics. *M2AN Math. Model. Numer. Anal.*, **41**, 315–331 (2007).

[31] M. Lewin, Solutions of the Multi-configuration Equations in Quantum Chemistry. *Arch. Rational Mech. Anal.*, **171**(1), 83–114 (2004).

[32] E. Lieb and B. Simon, The Hartree-Fock Theory for Coulomb Systems. *Commun. math. Phys.* **53** (1977), 185–194.

[33] P.-L. Lions, Solutions of Hartree-Fock equations for Coulomb systems. *Comm. Math. Phys.* 109 (1987), no. 1, 33–97

[34] P.O. Löwdin, Quantum Theory of Many-Particles Systems, I: Physical Interpretations by Mean of Density Matrices, Natural Spin-Orbitals, and Convergence Problems in the Method of Configurational Interaction. *Phys. Rev.* **97**, 1474–1489 (1955).

[35] C. Lubich, On variational approximations in quantum molecular dynamics. *Math. Comp.* **74**,765–779 (2005).

[36] N.J. Mauser and S. Trabelsi, L^2 analysis of the Multi-configuration Time-Dependent Equations. *Preprint.*

[37] H. Narnhofer and G.L. Sewell, Vlasov Hydrodynamics of a Quantum Mechanical Model. *Commun. Math. Phys*79 (1981), 9–24.

[38] H. Neunzert, Neuere qualitative und numerische Methoden in der Plasmaphysik, Lecture notes, Paderborn (1975).

[39] H. Spohn, Kinetic Equations from Hamiltonian Dynamics. *Rev. Mod. Phys.* 53 (1980), 600 – 640.

[40] H. Spohn, On the Vlasov hierarchy, *Math. Meth. Appl. Sci.* 4 (1981) 445-455.

[41] S. Trabelsi, Solutions of the Multi-configuration Time-Dependent Equations in Quantum Chemistry. *C. R. Math. Acad. Sci. Paris* **345** (3), 145–150 (2007).

[42] S. Zagatti, The Cauchy problem for Hartree–Fock time dependent equations. *Ann. Inst. H. Poincaré, Phys. Th.* **56**(4), 357–374 (1992).

[43] J. Zanghellini, M. Kitzler, T. Brabec, A. Scrinzi, Testing the multi-configuration time-dependent Hartree-Fock method. *J. Phys. B: At. Mol. Phys.*, **37**, 763–773 (2004).